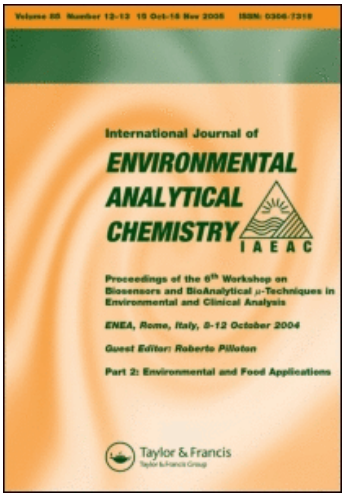

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Microextraction of Selected Polychlorinated Biphenyl Congeners and Dichlorodiphenyltrichloroethanes from Environmental Water and Analysis by Gas Chromatography-Electron Capture Detector

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MICROEXTRACTION OF SELECTED POLYCHLORINATED BIPHENYL CONGENERS AND DICHLORODIPHENYLTRICHLOROETHANES FROM ENVIRONMENTAL WATER AND ANALYSIS BY GAS CHROMATOGRAPHY —ELECTRON CAPTURE DETECTOR

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A simple method is described for the liquid-liquid microextraction of some polychlorinated biphenyls, DDT and some related compounds, from drinking tap water. The water sample is extracted with 1 mL of n-hexane for 10 minutes; the extraction is repeated and an aliquot for the combined extracts is injected directly into a capillary gas chromatograph equipped with an electron capture deterctor

The results indicate that the microextraction technique can be used for the quantitative recovery of PCBs and DDTs at their limits of quantitation. At 40 ng/L an average recovery close to 90% can be expected. The method could be particularly useful as a screening method for specific PCB congeners and related chemicals, in view of the relatively low cost of operation in terms of chemicals, apparatus and time with a minimum of organic solvent to be discarded or recycled.

KEY WORDS: Microextraction, PCBs, organochlorine pesticides, water samplers, gas chromatography.

INTRODUCTION

The large-scale use of polychlorinated biphenyls(PCBs) and dichlorodiphenyltrichloroethanes (DDTs) in North America has been curtailed in recent years. However, they are still found in many applications across the world and in many instances they find their way into the environment. Routine checks of environmental substrates, such as sediments and soils, reveal that DDTs and PCBs are still present although concentrations seem to be diminishing[1]. Nevertheless, environmental substrates are continuously monitored for these contaminants because their great persistence leads to bioaccumulation which in turn may have a negative impact on the health of living species[2].

PCBs and DDTs are usually extracted from water by solid phase adsorbent columns[3,4] or by liquid-liquid extraction[5]. Solid phase extraction requires 20–30 mL of solvent while liquid-liquid extraction may require several hundred mL. A common solvent used is n-hexane because it excludes many co-extractives that would otherwise interfere with the

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analysis. The use of a large volume of solvent is in itself a major drawback due to cost of purchase, handling and disposal. The time required and the equipment needed for evaporation are also costly.

The microextraction of chlorinated insecticides has previously been studied with a specially made extraction apparatus[6] using only 200 µL of solvent. However the need for special apparatus coupled with low recoveries (48–62%) and high variability probably explain why this particular method was never largely adopted.

This paper describes a liquid-liquid microextraction technique sustained by sufficient statistical data that shows that PCBs and DDTs may be recovered quantitatively from environmental water using a small volume of solvent (2 × 1 mL). An aliquot of the extract is injected directly into a gas chromatograph equipped with an electron capture detector (GC-ECD). The objective was to develop a method for PCBs and DDTs using a minimum amount of solvent which would be cost-saving in terms of time and amount of solvent used and discarded or recycled.

EXPERIMENTAL

Chemicals

Analytical standards of polychlorinated biphenyls, DDT and two related compounds were obtained from Ultra Scientific. A list is given in Table 1. Stock solutions (1 µg/µL) of the chemicals for STD-1 were prepared in ethyl acetate (Caledon Ltd) from pure standards then mixed together to give a solution containing 250 ng/µl of each. Mixed stock solutions for STD-2, 100 ng/µL in n-hexane, were obtained from Caledon Ltd. Water samples were fortified with a diluted solution (2 ng/µL) of the stock in methanol. Working standard solutions (200, 100, 50, 25, 10 pg/µL) used for reproducibility and other quantitation studies were prepared by dilution of the stock solution in n-hexane.

Table 1 List of Chemical studied.

Common name	*Chemical name*
PCB–10	1,6-dichlorobiphenyl
PCB–21	2,3,4-trichlorobiphenyl
PCB–26	2,3′,5-trichlorobiphenyl
PCB–28	2,4,4′-trichlorobiphenyl
PCB–49	2,2′,4,5′-tetrachlorobiphenyl
PCB–52	2,2′,5,5′-tetrachlorobiphenyl
PCB–86	2,2′,3,4,5-pentachlorobiphenyl
PCB–101	2,2′,4,5,5′-pentachlorobiphenyl
PCB–116	2,3,4,5,6-pentachlorobiphenyl
PCB–118	2,3′,4,4′,5-pentachlorobiphenyl
PCB–136	2,2′,3,3′,6,6′-hexachlorobiphenyl
PCB–137	2,2′,3,4,4′,5-hexachlorobiphenyl
PCB–138	2,2′,3,4,4′,5′-hexachlorobiphenyl
PCB–153	2,2′,4,4′,5,5′-hexachlorobiphenyl
PCB–180	2,2′,3,4,4′5,5′-heptachlorobiphenyl
p,p′-DDT	1,1,1-trichloro-2, 2-(4-chlorophenyl) ethane
p,p′-DDD	1,1-dichloro-2,2-bis (4-chlorophenyl) ethane
p,p′-DDE	1,1-dichloro-2, 2-bis (4-chlorophenyl) ethene

All solvents were pesticide grade or equivalent: n-hexane (Burdick and Jackson), iso-octane (BDH), cyclohexane (Fisher Scientific), hexanes (J. T. Baker).

The water used for recovery studies was doubly distilled and deionized. The water used to represent an environmental matrix was drinking tap water that came from an open air reservoir (lake) and which was chlorinated at the source by the City of Moncton, N.B., for purification purposes.

Instrumentation

A Perkin-Elmer Model 8700 gas chromatograph equipped with an electron capture detector (ECD-Ni63) and a fused-silica capillary column, 30 m × 0.32 mm (i.d.) containing 0.25 μm DB-5 (J. W. Scientific) was used. A one-metre pre-column (0.53 mm, i.d.) of deactivated fused-silica was present. Instrument settings were: initial temp., 55°C, increased to 160°C at 25°C/min, increased to 180°C at 2.5°C/min, increased to 214°C at 2.1°C/min, increased to 240°C at 10°C/min and kept there for 0.1 min. The injection port was set at 250°C and the detector at 350°C.

Method

This is the standard method developed in this study. Experimental conditions that differ are indicated with the data.

(a) *Fortification of water samples.* 50 μL of standard solution, 2 ng/μL in methanol, was added to 500-mL of water in a beaker and the solution was stirred with a magnetic stitrrer, for 10 min. at sufficient speed to produce a vortex to assure proper contact of the phases. Prior to extraction, 10 g of sodium chloride (commercial) was added to the water sample. The solution was then transferred into a 500-mL volumetric flask for extraction.

(b) *Extraction of water.* One mL of n-hexane was added to a 500-mL water sample in a 500-mL volumetric flask and the solution was stirred for 10 min (see above). After equilibration the extract was recovered with a Pasteur pipette. The extraction was repeated with 1 mL of n-hexane. The combined fractions yielded approx. 1.8 mL of extract which was diluted to 2 mL. The addition of a few drops of acetone during equilibration actually accelerates the separation of the phases and helps break down emulsions. The hexane extract obtained from this method was not dried before injection and no adverse effect on the cleanup or the chromatography was ever observed.

(c) *Quantitation.* A 1-μL aliquot was injected splitless into the gas chromatograph via a narrow bore injection liner. Quantitation was achieved by comparing peak heights with those of an external standard of 100, 50, 12.5 or 10 picograms.

(d) *Clean-up.* The extract was evaporated to 1 mL with nitrogen gas and applied to a FLORISIL SEP-PAK column, previously washed with 5 mL of n-hexane. The column was eluted with 4 mL of n-hexane and evaporated to 2 mL using nitrogen gas.

RESULTS AND DISCUSSION

The analysis of PCBs and DDTs using GC-ECD is still important because of its great sensitivity. However, in recent years the technique of GC-MS has become more popular particularly with the advent of new mass selective detectors which offer comparable

sensitivity to the ECD with added confirmation of species via mass spectral data[7]. In this study we have used the GC-ECD because of the non-availability of a GC-MS system and also because the primary objective of the experiment was to demonstrate the potential of the microextraction technique using standard solutions. In practice one would have to back-up the GC-ECD with a proper confirmation procedure such as GC-MS or re-analysis on a second GC column.

Since the early seventies one method for the quantitation of PCBs has been to compare the chromatogram with that of a mixture of commercial PCBs, commonly referred to as AROCHLORs. Several peaks of the sample may then be quantified by comparing peak heights or areas with those of an external standard and the results are often expressed as total PCBs[8]. With recent advances in capillary column technology greater specificity may be achieved and quantitation may then be obtained on the basis of several specific congeners representing those most likely to be found in nature[9–14].

For this study, one group(STD-1) of PCBs comprising the following congeners: 100(dichloro-), 21 and 26(trichloro-), 49(tetrachloro-), 86 and 116(pentachloro-) and 136(hexachloro-) and some DDT analogs were selected on the basis of their longtime use as a group in our laboratory for their quantitation in water. A second group(STD-2) of PCBs, namely, 28(trichloro-), 52(tetrachloro-), 101(pentachloro-), 118(pentachloro-), 153(hexachloro-), 137(hexachloro-), 138(hexachloro-), 153(hexachloro-) and 180(heptachloro-) congeners were selected because they are currently being used in Canada to compare various analytical procedures used by different laboratories in a check sample program.

Quality control

Initially the gas chromatograph was optimized for qualitative and quantitative performance within our quality control program. Initial tests were carried out with an analytical standard of 100 pg(STD-1). Minimum and maximum values of coefficients of variation for retention times were between 0.14 and 0.51% for p,p'-DDT and PCB-10, respectively. A typical chromatogram showing all eleven components of STD-1 is shown in Figure 1 (the values for STD-2 were well within that range) and a typical chromatogram is shown in Figure 2.

In terms of peak heights for 100 pg of each congener, the minimum and maximum values of the coefficients of variation for STD-1 were 1.70% and 9.50% for PCB-116 and PCB-10, respectively. For STD-2 the values were 2.22% and 6.78% for PCB-28 and PCB-137, respectively.

The response was linear between 1000 and 10 pg. With the P–E 8700 GC, 10 pg was considered to be a general limit of detection for all components of STD-1 with coefficients of variation between 9.20 and 26.9% for PCB-86 and PCB-136, respectively. For STD-2 the values varied between 3.55% and 10.5% for PCB-137 and PCB-52, respectively.

Recovery experiments

Previous experiments had shown that some organophosphorous pesticides (OPs) could be extracted from one litre of water using 1-mL of solvent but recoveries were low[15]. In particular the effects on the recoveries of various parameters, namely the presence of salt(NaCl), the type and volume of solvent, the extraction time and the volume of sample

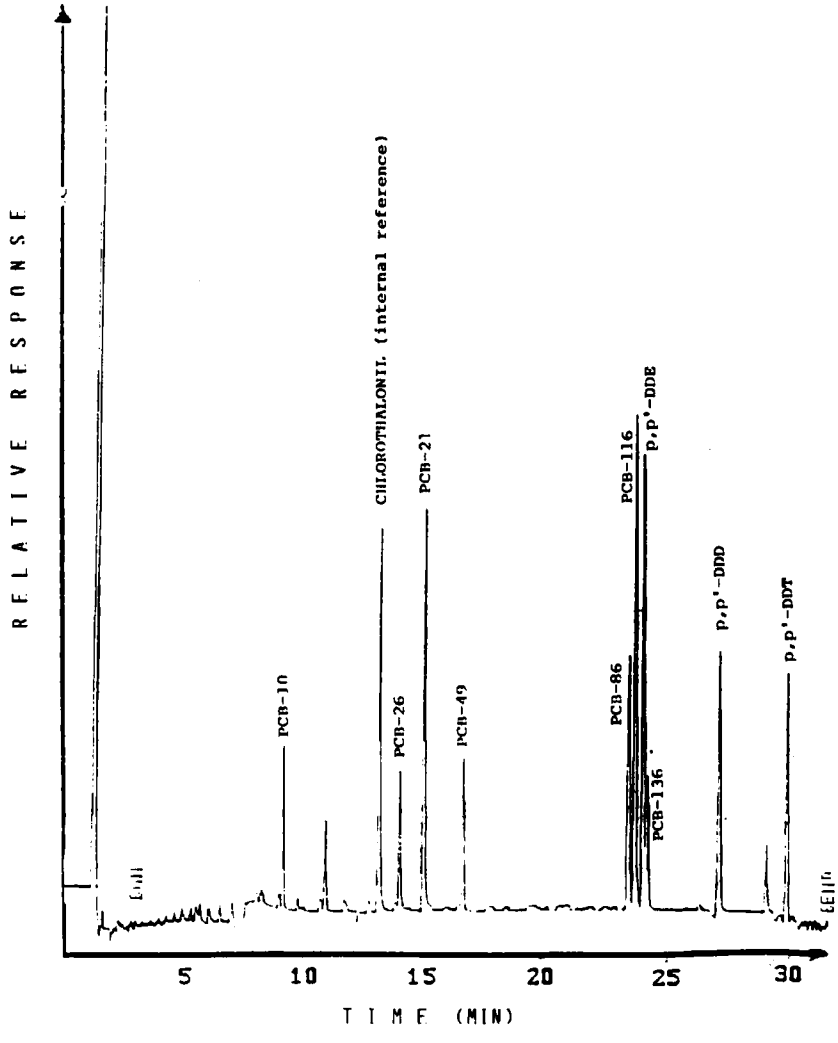

Figure 1 Chromatogram of a standard solution of PCBs and DDTs (STD–1) (100 pg of each component).

had been investigated. It was found that the addition of salt(1.0%) improved the recoveries by about 20% and that n-hexane was the preferred solvent because of reduced emulsions. After many experiments, it was accepted that the extraction of a 500-ml sample with 1-ml of n-hexane for ten minutes (repeated once) provided the best compromise for improved recoveries. Thus, five OPs were extracted from environmental water with n-hexane at the 0.1 ppb with an average recovery of 89.8 ± 6.1% (n=6).

These parameters were also investigated with PCBs and DDTs. Using STD-1, experiments with iso-octane and cyclohexane have shown that both solvents compared favorably with n-hexane in terms of recoveries but the latter showed less emulsions with environmental water. Thus, further experiments were carried out only with n-hexane. Initial experiments with one litre of water(single extraction) gave low recoveries (<60%) so further experiments were carried out with a 500-mL water sample at a concentration of 200 ng/L. Using 1 mL of n-hexane (single extraction) and an extraction time of five min.

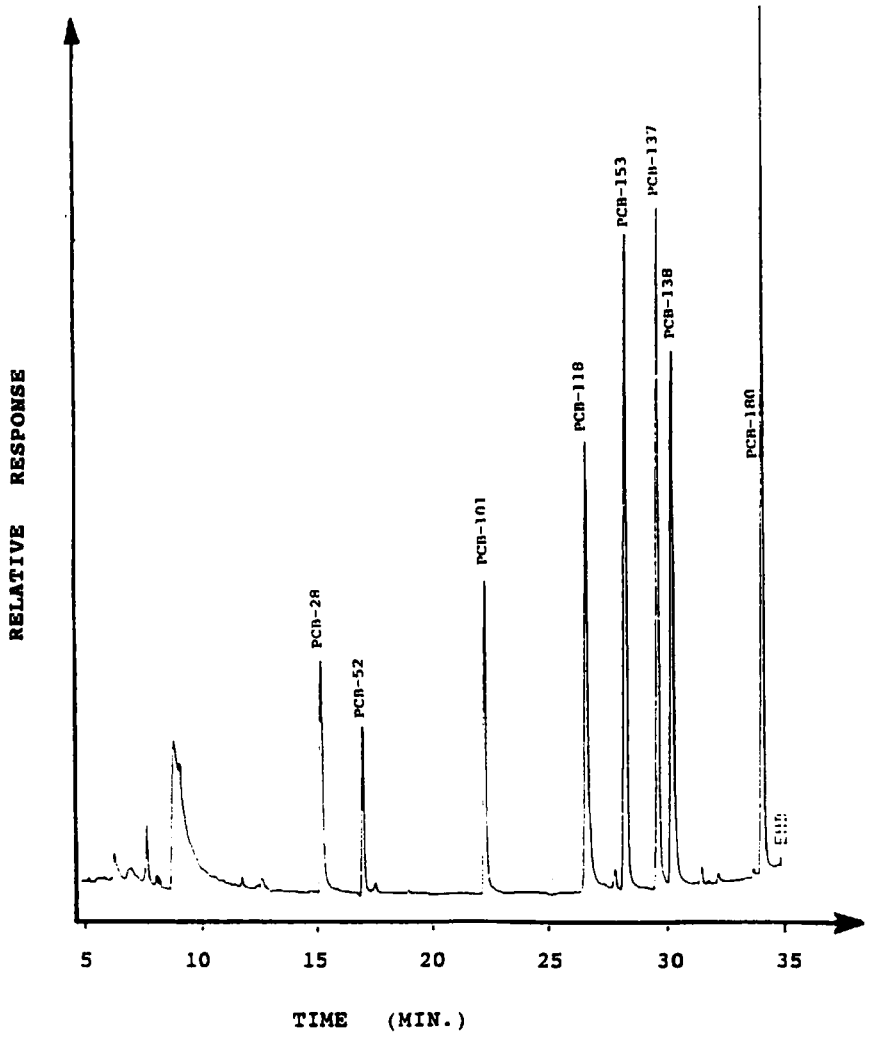

Figure 2 Chromatogram of a standard solution of PCBs and DDTs (STD–2) (100 pg of each component).

gave an average recovery of 63.2% as compared with 79.6% for an extraction time of 20 minutes. Subsequently, as with OPs it was determined that an extraction time of 10 min., repeated once, offered the best compromise in terms of time and volume of solvent.

Sodium chloride did not seem to have the same positive effect on the % recoveries of PCB's and DDT's as it did with OPs but it was found that the addition of 1–2% (by weight) was beneficial, especially with environmental water, because it helps break down emulsions.

Thus, under the conditions used in this study using distilled water, recoveries at 200 ng/L varied between 87.3% and 100%, as shown in Table 2. The average recovery was very high at 93.5% and the average coefficient of variation was reasonably low at 5.83%. Under the same conditions the results with STD-2 gave an average recovery of 87.0% with an average coefficient of variation of 4.81% as shown in Table 3. The difference between the two sets of results is not considered to be significant according to the t-test.

Table 2 Recovery of PCBs and DDTs (STD-1) from water.

	Distilled water[1] *(200 ng/L)*		*Tap water*[2] *(100 ng/L)*		*Tap water*[3] *(200 ng/L)*		*Tap water*[4] *(40 ng/L)*	
Chemical	$\bar{X}$	*C.V. (%)*	$\bar{X}$	*C.V. (%)*	$\bar{X}$	*C.V. (%)*	$\bar{X}$	*C.V. (%)*
PCB–10	87.3	9.52	92.3	3.59	72.0	7.31	86.5	15.0
PCB–26	87.9	7.44	77.6	8.07	62.2	9.20	N.D.	
PCB–21	89.1	6.22	86.9	7.61	87.3	8.67	int.	
PCB–49	87.8	7.16	81.4	3.75	75.0	10.2	78.4	14.0
PCB–86	100	4.02	81.8	6.27	76.0	7.93	95.7	9.81
PCB–116	96.3	1.66	84.6	3.43	72.0	8.18	90.2	10.5
p,p´–DDE	96.1	4.26	81.8	1.74	68.6	5.95	92.6	10.9
PCB–136	95.4	5.92	84.1	8.20	72.8	8.53	77.8	6.89
p,p´–DDD	98.1	5.96	77.2	3.29	98.1	6.43	107	8.44
p,p´-DDT	96.7	6.18	75.8	5.46	89.6	7.80	95.4	8.68
Average	93.5	5.83	82.4	5.14	77.4	8.02	90.5	10.5

Legend: [1] Volume of water, 500 mL; add 10 g NaCl; extract with n-hexane (2 x 1 mL, 2 x 10 min).
[2] Same as 1; add a few drops of acetone.
[3] Volume of water, 1 L; add 20 g NaCl; extract with n-hexane (as in 1); add acetone.
[4] Same as 2; N.D. = not detected; int. = interfering peak.

Table 3 Recovery of PCBs (STD-2) from water.

	Distilled water[1] *(200 ng/L)*		*Tap water*[2] *(200 ng/L)*		*Tap water*[3] *(50 ng/L)*	
Chemical	$\bar{X}$	*C.V. (%)*	$\bar{X}$	*C.V. (%)*	$\bar{X}$	*C.V. (%)*
PCB–28	86.1	7.6	73.6	6.82	int.	int.
PCB–52	86.0	6.33	76.7	5.95	76.2	7.02
PCB–101	85.7	2.99	76.5	7.05	81.9	8.63
PCB–118	88.8	2.51	74.5	13.0	87.6	9.86
PCB–153	85.9	3.26	69.4	10.9	80.7	9.80
PCB–137	84.8	5.19	69.9	10.6	84.2	12.8
PCB–138	87.3	6.07	69.1	9.04	91.7	14.0
PCB–180	90.2	5.07	65.7	13.5	84.9	11.3
Average	87.0	4.81	71.9	9.6	83.9	10.5

Legend: [1] Volume of water, 500 mL; andd 10 g NaCl; extract with n-hexane (2 x 1 mL, 2 x 10 min).
[2] Same as 1; andd a few drops of acetone.
[3] Volume of water, 1 L; add 20 g NaCl; extract with n-hexane (as in 1); add acetone.
[4] Same as 2; N.D. = not detected; int. = interfering peak.

With tap (environmental) water, the average recovery for STD-1(200 ng/L) was 78.6% and the average coefficient of variation was near 9%. The main problem encountered with environmental water was emulsions which made it difficult to recuperate most of the solvent. This problem was reduced by the addition of a few drops of acetone to the water sample during the extraction step. This did not seem to have any detrimental effect on the Florisil clean-up. Thus, with acetone the average recovery was 82.4% for STD-1 at 100 ng/L with an average coefficient of variation of 5.14% as shown in Table 2.

Although preceding experiments were carried out using only 500-mL of water to optimize recoveries, it is still feasible to work with the traditional 1-litre sample using a 1-L volumetric flask. Under the same experimental conditions the average recovery for 1-L samples (n=6) using STD-1 was 77.4% with an average coefficient of variation of 8.02% as shown in Table 2. These results were confirmed with STD-2 which gave an average recovery of 71.9% with an average coefficient of variation of 9% as shown in Table 3.

Limit of quantitation of the method

The limit of quantitation of a method is directly related to the limit of detection of the measuring instrument. In this study with the particular GC-ECD system used, a limit of detection of 10 pg/μL was accepted for the contaminants under study (see Quality Control) although particular compounds could have been detected at a lower limit. This translates into a limit of quantitation of 40 ng/L for the method developed in this study with a 500-mL water sample and a final volume of 2-mL for the extract. This is high compared to established methods but the objective in this study was to evaluate the potential of the microextraction technique not the limitation of the particular GC-ECD. Provided the water sample is relatively clean, all congeners may be recovered quantitatively from distilled water without interferences from co-extractives.

With the particular tap (environmental) water used in this study there were some interferences at 40 ng/L as shown in Table 2 for STD-1. Nevertheless, the average recovery for the other congeners and DDTs is quite acceptable at 90.5% with an average coefficient of variation of 10.5%. Results with STD-2 shown in Table 3, indicate an interference for PCB-28 but good recoveries for the other PCBs and a comparable average coefficient of variation as obtained with STD-1. It should be mentioned that the experiments with STD-2 were carried out one year after those for STD-1 and by a different person.

Thus, the present microextraction method for water is limited by two factors: (1) the limit of detection of our instrument; (2) the presence of co-extractives (see Figure 3a). Some instruments are quite capable of detecting amounts of PCBs 10 times lower but the limitation due to the presence of co-extractives would still prevail and worsen as the water becomes more contaminated. At this point it would become necessary to clean-up the extract. We have found that a contaminated extract can be conveniently cleaned-up by passing through a Florisil Sep-Pak. Some co-extractives remain at the beginning of the chromatogram (Figure 3b) but the latter part is rather clean. Under these conditions, we have found that all the PCBs in STD-2 could be detected without interferences (Figure 3c) and there is less variation for the peaks in the latter part of the chromatogram. Nevertheless, the results were similar with an average recovery of 84.6% and an average coefficient of variation of 9.12% as shown in Table 4.

CONCLUSION

Traditional liquid-liquid extraction methods may require up to 300 mL of solvent. Experiments with distilled water using such a large volume of solvent yielded an average recovery of 96.6% ± 8.28% (n=6) with STD-1 at 100 ng/L as compared with 82.4% ± 5.14% (n=6) with our method (see Table 4). Percentage recoveries are expected to be lower using a smaller volume of solvent but this drawback is largely surpassed by the

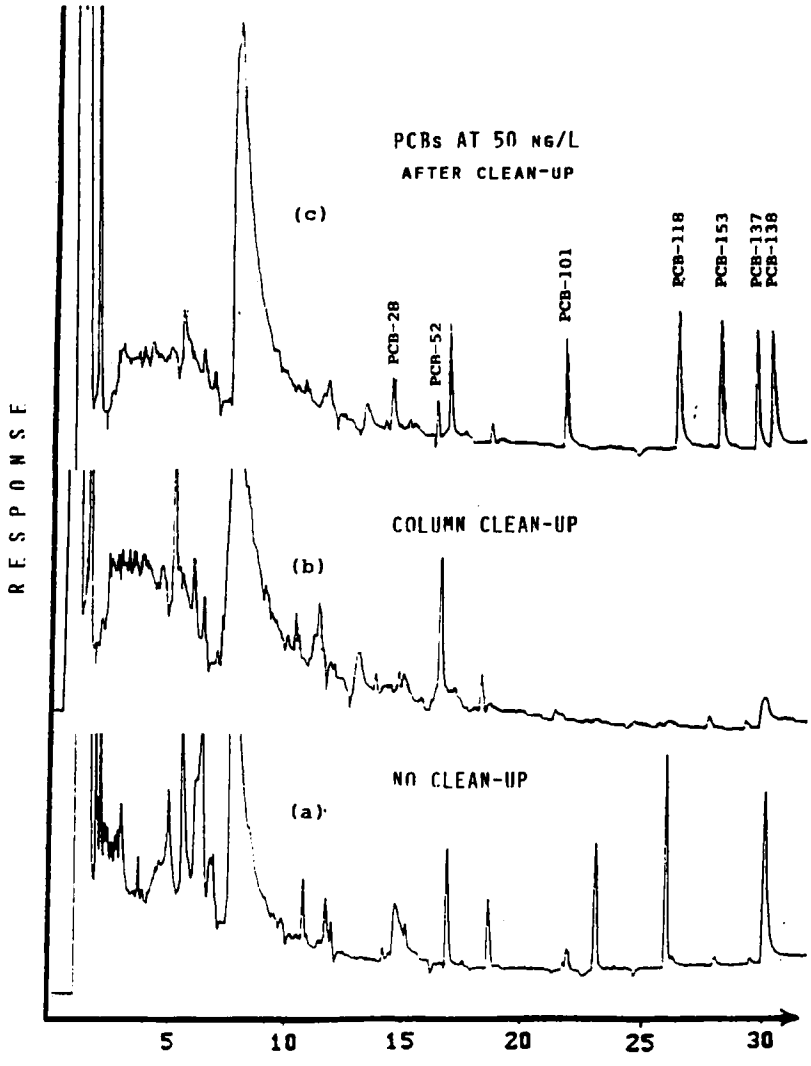

Figure 3 Chromatogram of water extract (a) no clean-up (b) after clean-up with Florisil (c) fortified water extract (50 ng/L) after clean-up with Florisil.

Table 4 Recovery of PCBs (STD-2) (50 ng/L) from environmental water after clean-up.

Chemical	*1*	*2*	*3*	*4*	*5*	*6*	$\bar{X}$	*S*	*C.V.(%)*
PCB–28	90.9	100	84.6	76.9	87.0	90.9	88.4	7.69	8.70
PCB–52	101	84.6	75.0	83.3	84.6	79.2	84.6	8.85	10.5
PCB–101	86.4	81.8	67.3	82.6	84.4	63.9	77.7	9.59	12.3
PCB–118	95.8	71.4	76.2	85.7	90.5	81.0	83.4	9.07	10.9
PCB–153	88.9	77.5	88.9	80.6	76.3	75.0	81.2	6.25	7.70
PCB–137	89.2	83.9	92.1	81.1	84.8	83.7	85.8	4.06	4.43
PCB–138	107	88.1	93.8	94.4	87.5	78.1	91.4	9.60	10.5
PCB–180	89.7	87.2	85.4	76.9	90.0	74.4	83.9	6.68	7.96
Average							84.6		9.12

savings in terms of quantity of solvent used (2-mL instead of 300-mL) and the lesser time involved. Less solvent used also means less solvent to discard or recycle at a cost. With proper attachments the procedure could certainly be automated. More work is needed to extend the method to other PCBs and other contaminants. Present work involves OCs and chlorinated benzenes usign GC-ECD and GC-MS. Nevertheless, the experiments carried out to date definitely establish the potential of using the liquid-liquid microextraction approach.

Finally, one question that needs to be addressed is that of co-extractives from an overly contaminated environmental sample (such as from sewage water or lagoon). We are presently testing the micro-extraction approach for PCBs in a more difficult substrate namely, saltwater mussels. The hexane extract is obviously contaminated but we have found that interfering co-extractives can be conveniently removed by passing through a neutral alumina column (4 cm × 1 cm i.d.). An extract from a contaminated effluent sample could also be treated in the same manner.

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